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(57) Abstract

A multilayered ductile product is disclosed comprising a rapidly solidified, homogeneous alloy foil metallically bonded to a substrate, wherein the substrate is capable of undergoing a substantial degree of plastic deformation without substantial degradation of its ductility. The product is particularly useful as brazing strip. Also disclosed is a roll bonding process for producing continuous ductile brazing strip.

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PLYMETAL BRAZING STRIP

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to the production of flexible multilayered strip and, in particular, to the production of flexible multilayered brazing foils formed of rapidly solidified homogeneous metal foil joined to a ductile substrate.

Background of the Invention

Brazing is a process for metallurgically bonding materials, often of dissimilar compositions, to each others at temperatures above about 450°C. Typically, a filler metal that has a melting point lower than that of the base material parts to be joined is interposed herebetween and the assembly is then heated to a temperature sufficient to melt the filler metal. Upon cooling, a strong joint is formed.

The process of brazing is commonly employed in the manufacture of a wide variety of products such as heat exchangers, cemented carbide tipped tools, bicycle frames, electrical products, etc. In order to accommodate the various configurations of joints which require brazing, brazing fillers are employed in powder, ribbon, wire or wrought form.

Improved brazing foils have been formed by rapid solidification techniques. These foils possess the ability to substantially reduce the number of failed joints because of improved homogeneity resulting from the rapid solidification process. Examples of such

improved materials are disclosed in U.S. Patent Nos. 4,448,852 and 4,489,136.

However, rapidly solidified brazing foils exhibit loses in relative ductility as the foil thickness increases and especially at foil thicknesses of greater than about 75-100 μ m. Accordingly, there are applications which, because of the configurations of the brazed joint (especially those requiring a brazing filler-metal thickness larger than about 75 μ m) require either special handling of the rapidly solidified brazing foil or, in some instances, require the selection of an alternative, inferior brazing material.

There remains a need in the art to further expand the utility of rapidly solidified brazing foils by reducing, and preferably eliminating, special handling requirement, and enhancing their utility in applications requiring thick brazements.

SUMMARY OF THE INVENTION

The present invention is directed to multilayered products, in particular multilayered brazing foils, which comprise a rapidly solidified, homogeneous alloy foil metallically bonded to a substrate, wherein the substrate is capable of undergoing a substantial degree of plastic deformation without any substantial degradation of its ductility, and wherein the integrity of the foil layer is maintained.

In addition, the present invention is directed to a process for producing multilayered products, in particular multilayered brazing foils, which comprises the steps of: arranging a rapidly solidified, homogeneous alloy in contact with a substrate capable of undergoing a substantial degree of plastic deformationswithout experiencing a substantial degradation of the ductility thereof; and applying heat and pressure to the alloy and substrate at a

temperature and pressure in an amount and for a time sufficient to cause the substrate to undergo plastic deformation and to create metallic bonding between the alloy and the substrate. In the most preferred embodiment, bonding is accomplished by a roll bonding process to produce continuous, multilayered brazing strip.

Further, there is provided in accordance with the invention an improved process for brazing parts, the process comprising the steps of arranging at least two parts relative to each other to define a gap therebetween, interposing in the gap between the parts a multilayered brazing filler material comprising a layer of rapidly solidified, homogeneous alloy foil metallically bonded to a substrate capable of undergoing substantial plastic deformation without substantial degradation of the ductility thereof, heating at least the filler material to melt at least the foil and to cause the parts to be joined, and then cooling the filler material to produce a brazement.

DETAILED DESCRIPTION OF THE INVENTION

In any brazing process, the brazing material must meet a variety of criteria in order to be acceptable for use in the process. For example, the brazing material must have a melting point that is sufficiently high to maintain its integrity and physical properties over the entire range of service requirements of the metal parts being brazed. However, the melting point must not be so high as to make difficult the brazing operation. Further, the filler material must be compatible, both chemicallly and metallurgically, with the parts being brazed. Morever, the brazing material should be homogeneous; that is, it should have a substantially uniform composition in all dimensions. In addition, the brazing material must be ductile to enable it to be formed to accommodate the size and shape of the joint gap to be brazed. Finally,

the brazing material must be thick enough to provide sufficient filler metal to fill completely the gap.

We have invented a multilayered product comprising a rapidly solidified, homogeneous alloy foil metallically bonded to a substrate, wherein the substrate is capable of undergoing a substantial degree of plastic deformation without substantial degradation of its ductility. Multilayered metallic products are generally referred to as "plymetal" parts.

Rapidly solidified, homogeneous alloy foils have been produced for a number of years by a process referred to as rapid solidification technique. See, for example, U.S. Patent Nos. 4,448,852 and 4,489,136. Typically, the process comprises the steps of selecting a particular composition of the requisite elements in the desired proportions, melting and homogenizing the same, and depositing the molten compositions onto a chill surface, such as rapidly rotating cylinder, to quench the composition.

Rapid solidification as used herein means the application of a quench rate of at least about 10^5°C/sec. The products resulting from this process may be crystalline or amorphous, but regardless of their structure, they are homogeneous. Furthermore, the products are in foil form; that is, they have a thickness that is small relative to the width and length of the product. Most preferably, the foil is in the form of ribbon.

In accordance with the present invention, the rapidly solidified, homogeneous foil is metallically bonded to a substrate. The substrate is formed of a material which is capable of undergoing a substantial degree of plastic deformation without substantial degradation of its ductility. In practice, the degree of plastic deformation ranges from a few percent to 10-20 percent or more. Substrates within the scope of the invention include Cu and Cu-base alloys, Cu-Ag-base

alloy, Fe and Fe-base alloys and Ni and Ni-base alloys. Most preferably, the substrate is matched to the foil to which it is to be bonded. For example, Cu-base alloy foils would most preferably be bonded to Cu or Cu-base alloy substrates.

Essential to the production of multilayered products within the scope of the present invention is the creation of metallic bonds between the foil and the substrate. As is well known in the art, metallic bonds are created by the sharing of electrons by groups of atoms, creating what is sometimes referred to as an electron cloud of free moving electrons. In the present invention, the existance of a composition gradient between the foil and substrate, which enhances the creation of such electron cloud, coupled with plastic deformation of the substrate at an elevated temperature yields an essentially void free, continuous interface between the foil and substrate and creates to produce a strong metallic bond at the interface.

Multilayered products within the scope of the invention are, most preferably, brazing strips. The brazing strips of the present invention overcome a long-felt need in the industry to produce thick, ductile brazing strip from compositions which are inherently brittle in conventional form or in thick ($\gtrsim$ 100 μm) rapidly solidified foil from. (Most brazing alloys contain a large concentration of metalloid elements such as Si, B, and P which form brittle intermetallic compounds upon crystallization.) The present invention advantageously utilizes the plasticity and inherent ductility in the substrate to produce a multilayered product which has ductility substantially equal to he ductility of the substrate. Thus, the invention is particularly useful in brazing applications which require filling a gap of 100 μm or more. Moreover, the multilayered brazing strip enhance the ability to braze certain dissimilar materials. For

example, in the bonding of carbide layers onto steel shank tools, the prior art employed expensive silver-base brazing filler metal to braze the carbide to the steel. However, because the thermal expansion coefficient of the carbides and steel are so different, internal stresses in the brazement are quite high and can lead to premature failure. With the present invention, a three-layered strip of a substrate, such as copper, sandwiched between rapidly solidified homogeneous-brazing alloy is used because the substrate accommodates the difference in stresses between the carbide and the steel while maintaining the service thermal and strength requirements of the tool.

Another advantage to the production of thick brazing filler products is the elimination of the need for adhering together multiple strips of rapidly solidified material through the use of binders which could contaminate the brazement and/or create voids therein. With the present invention, one can, for the first time, produce brazing filler strips of rapidly solidified brazing foil in thickness of 100 μm or greater. Morever, because of the loss in ductility of rapidly solidified alloys as they approach 100 μm or more in thickness, the present invention provides thick brasing strip which has all the advantages associated with rapidly solidified brazing foil.

The process of making the products of the present invention comprises the steps of arranging the foil in contact with the substrate and, thereafter, applying heat and pressure to the foil and substrate to cause the substrate to undergo plastic deformation and create metallic bonding between the foil and the substrate.

In its broadest concept, the foil and substrate can be brought into contact in any of a variety of ways such as by laying the foil on top of the substrate by hand or, in the most preferred embodiment, by providing

the substrate and foil as continuous spools from which strip is continuously fed into contacting relationship at a location at which bonding is to occur.

Bonding can be created by means of any suitable apparatus which is capable of applying heat and pressure in accordance with the teachings hereinafter. To that end, conventional cladding equipment can be employed. Most preferably, roll bonding apparatus employing heated rolls is used to produce continuous brazing strip. With such apparatus, the substrate and foil are fed continuously past heated rolls designed and arranged to provide substantially constant temperature and pressure to the substrate and foil in order to bond the same.

The temperature at which bonding is effected is dependent upon the structure of the rapidly solidified foils. For amorphous foil (i.e., foil which is at least 50% amorphous by x-ray diffraction), the temperature of bonding must be equal to or greater than the crystallization of the amorphous foil. For crystalline foil (ie., foil which is less than 50% amorphous by X-ray diffraction), the temperature of bonding must be at least about 0.4T, where T is the melting temperature of the alloy in degree Kelvin, K.

The pressure applied to the layers must be sufficient to cause plastic deformation of the substrate in an amount necessary to create an essentially continuous, void-free interface between the foil and the substrate. Accordingly, while the pressure will vary depending upon the substrate material employed, it is preferred that a force of at least about 0.75 MN be used. In particular, for roll bonding (500 mm O.D. rolls), we prefer to employ a separating force of between 0.75 MN and about 2.5 MN, although lower and higher pressures can be used.

The time during which the heat and pressure are applied must not be so long as to degrade the integrity

and ductility of the multilayered product. However, because of the wide variety of temperature and pressures which may be used in our process, it is not possible to quantify the time at temperature and pressure, except by reference to product integrity. To those of ordinary skill in the art, processing conditions are sufficient when the multilayered product does not evidence substantial degradation upon bending or stressing of the product.

An additional feature of the process is the step of cooling the bonded product. Most preferably, the product is cooled by employing air or a non-oxidizing medium such as nitrogen or an inert gas. The cooling most preferably occurs immediately after completion of the bonding step to avoid oxidation of the surface of the product which may affect product utility as a brazing strip.

In accordance with the present invention, processes for brazing parts comprise the steps of arranging at least two parts relative to each other to define a gap therebetween, interposing in the gap a multilayered brazing filler material comprising a layer of rapidly solidified, homogeneous alloy foil metallically bonded to a substrate capable of undergoing substantial plastic deformation without substantial degradation of the ductility thereof, heating at least the filler material to melt at least the brazing foil layer of the strip and to cause the parts to be joined, and thus cooling the filler material to produce a brazement.

The multilayered products of the present invention are superior to prior art products employed as brazing foils for all of the reasons described heretofore. While the invention has been described primarily by reference to two layered products, it should be quite evident that particularly useful products are those which include more than two layers,

e.g., three layers composed of a substrate sandwiched between two rapidly solidified foils as described heretofore.

The following examples are provided in order to illustrate the scope of the inventions but are not intended to limit the scope of the invention to anything less than is disclosed hereinabove.

Example 1

A multilayered brazing strip was produced using an electrolytic tough-pitch copper substrate and a BAg-3 (American Welding Society Designation) microcrystalline alloy. BAg-3 microcrystalline alloy was produced by remelting Handy and Harman's Easy Flo-free™ alloy in a quartz crucible and casting by a planar flow rapid solidification technique. The center was 2 plies of 25 mm x 75 μm thick copper ribbon. The outer layers were made from 25 mm x 75 μm ribbon of BAg-3 brazing alloy. There BAg-3 layers had, prior to rolling, microhardness of 230 and 260 HV (Vickers microhardness units), respectively. The copper ribbon had a microhardness of 120 HV. In this case, the copper ribbon is about twice as ductile and malleable as the BAg-3 alloy.

The strip was produced by high temperature consolidation on a Stanat 6" x 6" rolling mill. At 178 kN force, well bonded material was produced at rolls temperature of 380-400°C and at .03-.05 m/s rolling rate. By using two copper plies together as the substrate, a strip with the commercially desired thickness of 300 m was produced. Strips of 360 mm length were produced.

Example 2

Ribbon, 38 μm thick, of an alloy designated as MBF-2005 (having a composition within the range of compositions disclosed in U.S. 4,489,136) was bonded to both sides of a 406 μm thick (16 gauge) copper strip. The consolidation was carried out in a Canadian Iron

Foundry, 2-high, heated rolling mill with 500 mm diameter cast steel rolls. The 101 mm wide brazing alloy formed the outer layers while the 108 mm wide, soft copper composed the center core. Roll speed was held at 5 m/min, roll temperature at 490°C, while rolling pressure was 2.0 MN. A well bonded multilayered strip was produced.

Example 3

Smaller strips of brazing metal alloy were used to build a wider multilayered plymetal strip. With conditions similar to that in Example 1, a 50 and a 100 mm wide MBF-2005 alloy ribbons were consolidated side by side on both surfaces of a 150 mm wide, 406 μm thick copper strip. Well bonded plymetal was produced at a speed of 10 m/min and with a rolling pressure as low as 0.6 MN. A 2.4 meter multilayered strip was produced.

Example 4

Using the same heating rolling mill as described in Example 2, above, 100 mm wide x 38 μm thick ribbons of alloy MBF-2005 were clad on both sides of a 150 mm wide x 127 μm thick copper core. At conditions of 5 m/min rolling speed, 490°C rolls temperature and 1.6 MN rolling pressure, twenty well bonded strips of plymetal were produced. Good metallurgical bonding between the copper substrate and MBF-2005 alloy and a fine uniform crystalline structure of the MBF-2005 alloy layers resulted. Differential thermal analysis of this plymetal strip was done on a Perkin-Elmer 1700 DTA analyzer in order to determine the melting characteristics of this strip. The strip characteristics are essentially the same as the characteristics of an MBF-2005 single ribbon when measured in the brazing temperature range. The presence of a metallurgically-bonded copper core does not change the strip melting behavior of the low melting MBF-2005 constituent layers.

Example 5

In the same equipment and under similar conditions as in Example 3, separate 25 and 50 mm wide x 38 μm thick ribbons of MBF-2005 alloy were bonded to both sides of a 25 mm wide x 127 μm thick copper core. At conditions of 5 m/min rolling speed, 520°C roll temperature and 1.3 MN force, twenty well-bonded, 300 mm long strips of plymetal were produced.

Example 6

Two 100 mm wide, 50 μm thick ribbons of copper-tin (90/10) brazing alloy (designated MBF-2004B) were clad on both sides of a 100 mm wide, 37 μm thick copper strip. The same equipment as in Example 3 was used and the production conditions were 3.0 m/min rolling speed, 525°C rolls temperature and 1.45 MN roll pressure. During some tests, the exiting strip was cooled by compressed air. The addition of the cooling step produced a brighter, shinier, oxidation free strip surface. Strong metallurgical bonding was achieved with this process as well.

WE CLAIM:

1. A multilayered ductile product comprising a rapidly solidified, homogeneous alloy foil metallically bonded to a substrate, wherein the substrate is capable of undergoing a substantial degree of plastic deformation without substantial degradation of its ductility.

2. The multilayered product of claim 1 wherein the alloy foil is a brazing alloy foil.

3. The multilayered product of claim 2 wherein the ductility of the substrate is greater than the ductility of the foil.

4. The multilayered product of claim 2 wherein the multilayered strip is at least about 50 μm thick.

5. The multilayered product of claim 2 further comprising a metallic layer bonded to the foil on a side of the foil remote from the substrate.

6. The multilayered product of claim 2 wherein the product is a continuous strip.

7. The multilayered product of claim 2 further comprising a rapidly solidified, chemically homogeneous alloy layer metallically bonded to the substrate on a side of the substrate remote from the alloy foil.

8. The multilayered product of claim 2 wherein the substrate is selected from the group of Cu,Fe and Ni metal, Cu-base alloys, Cu-Ag base alloys, Fe-base alloy, and Ni-base alloys.

9. The multilayered product of claim 2 wherein the substrate is a copper-base alloy and the foil is an alloy of a composition suitable for brazing Cu and Cu-base alloys thereof.

10. The multilayered product of claim 2 wherein the substrate is steel and the alloy foil is an alloy of a composition suitable for brazing Fe and Fe-base alloys thereof.

11. A process for producing a multilayered product, the process comprising the steps of:

a) arranging a rapidly solidified, homogeneous alloy in contact with a substrate capable of undergoing a substantial degree of plastic deformation without experiencing substantial degradation of the ductility thereof; and

b) apply heat and pressure to the alloy and substrate at a temperature and pressure in an amount and for a time sufficient to cause the substrate to undergo plastic deformation and create metallic bonding between the alloy and the substrate, but not so long as to degrade the integrity and ductility of the multilayered product.

12. The process of claim 11 wherein the alloy is a brazing foil.

13. The process of claim 12 wherein the alloy is amorphous and wherein the alloy and substrate are heated to a temperature equal to or greater than the crystallization temperature of the amorphous alloy.

14. The process of claim 12 wherein the alloy is crystalline and wherein the alloy and substrate are heated to a temperature of at least about 0.4 T, where T is the melting temperature of the alloy in degree Kelvin, K.

15. The process of claim 12 further comprising the steps of cooling the product after the heating step with a cooling gas.

16. A process for roll bonding a foil to a substrate to produce a multilayered product, the process comprising the steps of:

a) supplying to a gap defined between a pair of opposed rolls a foil of rapidly solidified, homogeneous alloy;

b) supplying to said gap in contacting relationship with said foil a metallic substrate;

c) applying heat and pressure through said rolls to plastically deform the substrate and effect metallic bonding between the foil and substrate; and

d) cooling the bonded product.

17. The process of claim 16 wherein the foil and substrate are continuous strips, the supply of each is continuous and the bonding is carried out continuously to produce continuous product.

18. The process of claim 16 wherein the force applied to the foil and substrate is maintained substantially constant and wherein the force applied to the rolls ranges from between about 0.75MN to about 2.5MN.

19. The process of claim 18 wherein the alloy is amorphous and the temperature of heating is greater than or equal to the crystallization temperature of the alloy.

20. The process of claim 18 wherein the alloy is crystalline and the temperature of heating is at least about 0.4T, where T is the melting temperature of the alloy in degree Kelvin, K.

21. The process of claim 11 wherein the alloy undergoes substantially no plastic deformation.

22. The process of claim 18 wherein the alloy undergoes substantially no plastic deformation.

23. A process for brazing parts, the process comprising the steps of:

a) arranging at least two parts relative to each other to define a gap therebetween;

b) interposing in the gap between the parts a multilayered brazing filler material comprising a layer of rapidly solidified, homogeneous alloy foil metallically bonded to a substrate of a material capable of undergoing substantial plastic deformation